

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Appln. No.: 10/528,527  
Applicant: Cornelis Martinus Lok  
Filed: March 18, 2005  
Title: PROCESS FOR PREPARING COBALT CATALYSTS ON TITANIA SUPPORT  
T.C./A.U.: 1793  
Examiner: Cam N. Nguyen  
Confirmation No.: 8287  
Docket No.: JMYS-123US

Commissioner for Patents  
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**DECLARATION OF CORNELIS MARTINUS LOK PURSUANT TO 37 C.F.R. §1.132**

I, Cornelis Martinus Lok, being duly warned that willful false statements and the like are punishable by fine or imprisonment or both, under 18 U.S.C. §1001, and may jeopardize the validity of the patent application or any patent issuing thereon, state and declare as follows:

1. All statements herein made of my knowledge are true and statements made on information and belief are believed to be true.
2. I am of Dutch nationality and gained the Drs and PhD degrees in chemistry from the University of Leiden, Holland in 1969 and 1972 respectively.
3. I then worked continuously until my retirement in March 2008 in the field of catalysis, primarily hydrogenation catalysis. Thus from 1973 to 1986 I worked in the Research department of Unilever NV at Vlaardingen, Holland, a.o. as Section Manager Catalysis & Porous Structures, and from 1986-1992 I was head of Development at Unichema GmbH at Emmerich, Germany. From 1992-1997 I worked for Unilever Plc at Port Sunlight, England, as Catalyst Programme Manager and joined Crosfield Ltd., at Warrington, England in 1997 as the Catalysts Group Research Manager. From 1997 to my retirement in March 2008 I was a Senior

Research Manager responsible, amongst other things, for Co and Ni catalysts for hydrogenation and Fischer-Tropsch processes.

4. The Crosfield Ltd catalysts business was acquired by Imperial Chemical Industries PLC in 1997 and then the ICI catalysts business was acquired by Johnson Matthey PLC in 2002. I worked for Johnson Matthey PLC until my retirement in March 2008.
5. I am the named inventor on this patent application.
6. I have read and am familiar with the contents of this patent application and U.S. Patent No. 7,452,844 (Hu et al.).
7. The experiments described herein were conducted under my supervision and surprisingly show cobalt crystallites that are considerably smaller when made by the process of the present invention yet still effective in Fischer-Tropsch reactions as compared with the teachings of Hu et al., which describes catalysts with a cobalt crystallite size less than about 50Å, which deactivate rapidly in the Fischer-Tropsch process.
8. Cobalt on titania catalysts were prepared according to the method of the present application using cobalt ammine carbonate (catalysts A & B). Two titania powders were used: one rutile and the other anatase. The catalysts prepared according to the claimed invention produced cobalt oxide without calcination and instead were simply dried. The amount of cobalt in the dried samples was determined.
9. X-ray diffraction (XRD) measurements were taken in order to determine the cobalt oxide and titania phases and also to determine the apparent cobalt oxide crystallite size prior to reduction. In each case,  $\text{Co}_3\text{O}_4$  was found to be the only cobalt compound present in the dried samples.
10. Reduction was achieved using standardised conditions with hydrogen at 425°C. Cobalt surface areas were measured by hydrogen chemisorption on the reduced catalysts at 150°C.

Catalyst	TiO <sub>2</sub>	Co level (wt%)	Co Surface Area (m <sup>2</sup> /g reduced catalyst)	Co Surface Area (m <sup>2</sup> /g cobalt)	Co <sub>3</sub> O <sub>4</sub> crystallite size (Angstroms)
A	Anatase	22.8	5.9	25.9	28
B	Rutile	31.6	9.0	28.5	36

11. These results show Co<sub>3</sub>O<sub>4</sub> crystallites considerably smaller than those in Hu et al. (e.g., less than about 40Å). Figure 6 of Hu et al. shows the size of the Co<sub>3</sub>O<sub>4</sub> crystallites on an order of magnitude greater than 60 Angstroms. In fact, Hu et al. discourages a cobalt crystallite size of less than about 50 Angstroms due to negative effect in Fischer-Tropsch processes:

The metal crystallite size is inversely proportional to the metal dispersion, i.e., as the crystallite size decreases, the dispersion increases. However, there is a practical lower limit to the crystallite size because at very small crystallite sizes, sintering occurs during use destroying the utility of the catalyst. For the cobalt-based F-T catalyst, studies have shown that when the cobalt crystallite size is less than about 50Å diameter, the crystallites appear to deactivate rapidly in the presence of water, which is typically present in the Fischer-Tropsch process (see Iglesia, p 64). In a preferred embodiment of the invention, the cobalt oxide crystallite size, as determined based on line broadening of X-ray diffraction patterns using methodology known in the art, is greater than about 40Å diameter, and is preferably less than about 200 Å. More preferably, the crystallite size is from about 50Å to about 150Å, and most preferably, the crystallite size is from about 50Å to about 120Å. *Hu et al. col. 6, lines 27-43.*

12. Unlike the disclosure of Hu et al., we have shown catalysts in accordance with the invention that have crystallites smaller than 40 Angstroms, which are surprisingly effective in Fisher-Tropsch catalysts. See, e.g., Example 12 in the instant application.



Cornelis Martinus Lok

Date:

9 January 2010